



PATENT SPECIFICATION

NO DRAWINGS

960,493

Date of Application and filing Complete Specification: Dec. 12, 1961.

No. 44530/61.

Application made in United States of America (No. 76161) on Dec. 16, 1960.

(Patent of Addition to No. 956,802 dated Aug. 10, 1960.)

Complete Specification Published: June 10, 1964.

© Crown Copyright 1964.

Index at acceptance:—C5 G1A1

International Classification:—C 10 g

COMPLETE SPECIFICATION

Motor Fuel Compositions containing Polyolefin Substituted Succinimides of Tetraethylene Pentamine

We, CALIFORNIA RESEARCH CORPORATION, a corporation duly organized under the laws of the State of Delaware, United States of America, and having offices at 200 Bush Street, San Francisco 4, California, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention pertains to motor fuel compositions having incorporated therein metal-free detergents. In particular, this invention pertains to spark-ignition internal combustion engine fuels containing the particular metal-free detergents, polyolefin substituted succinimides of tetraethylene pentamine.

Alkenyl succinic anhydrides and numerous derivatives thereof are well-known in the art. For example, alkenyl succinic anhydrides in which the alkenyl radical contains from 5 to 20 carbon atoms are taught as corrosion inhibitors in lubricating oil compositions. Also, products obtained by reacting such alkenyl succinic acid anhydrides with mono-amines are taught as ferrous corrosion inhibitors for lubricating oil compositions.

However, the above known alkenyl succinimides are not useful as detergents. In contrast thereto, the polyolefin substituted succinimides which are described herein are compounds which are useful as detergents in internal combustion engine fuel compositions.

Present day spark-ignition engines operate at high speeds and high compression ratios. When used in the so-called city stop-and-go driving, which includes the greater part of the driving conditions for a large percentage of today's automobiles, these engines do not reach the most efficient operating temperature. Under city driving conditions, deposits accumulate in carburetors and in the fuel induction systems of automobile spark ignition engines and in stationary spark-ignition engines whenever they have to run a considerable time at idle, for instance, in the operation of generator sets in electric power plants and the like industrial installations.

With regard to deposits on carburetors of spark-ignition engines, the critical accumulation point for these deposits is on the wall of the throttle body of the carburetor adjacent to the throttle plate, whose position controls the idle air-fuel ratio. As these deposits accumulate, the air flow at idle is restricted with no change in fuel flow and an over-rich mixture results, causing erratic idling and engine stalling. In order to compensate for the presence of these deposits, the throttle must be opened slightly by increasing the idle speed adjustment, which, although allowing more air flow, automatically supplies more fuel. This requires a fuel correction by changing the idle fuel adjustment screw a compensating amount. The amount of idle fuel adjustment required to maintain satisfactory idle performance is an indication of the deposit build-up. Furthermore, deposits will often form in the idle, vacuum-breaking, air passageway, causing restriction, which allows the manifold vacuum to draw more gasoline into the engine, again causing rich idle and engine stalling.

It has been established that the primary source of these carburetor deposits is provided by the contaminants in the intake air of the engine when operating at idle. The greatest source of these intake air contaminants is engine blowby, which accounts for approximately one-half of the deposits. The term "blowby" refers to air-fuel mix-

5 pure gases and burned gases which have been compressed and leaked past the piston rings from the combustion chamber into the crank-case. At idle, under the engine hood of an automobile, or within the housing of a stationary engine, a large portion of these "blowby" gases penetrates into the engine's air intake. Exhaust from other vehicles, dust, and other air pollutants, further contribute to the formation of deposits. 5

10 In addition to the aforementioned deposits, further deposition occurs in the intake manifold and ports, and on the underside of the intake valve heads of spark-ignition engines due to causes distinct from those previously discussed. One of the major sources of these supplementary deposits is the phenomenon known as "puff back", which is the passage of combustion gases from the combustion chamber of the engine through the intake valves into the intake ports immediately prior to the intake stroke. This "puff back" carries combustion deposits which tend to lay down on the surfaces of the intake ports and valves. Additional deposits, particularly those formed in the intake manifold, are derived from existent gums present in the gasoline, the decomposition of the anti-knock lead alkyl additive, such as tetraethyl lead, small amounts of gums formed by oxidation of the gasoline in the intake manifold, exhaust gases and road dust. 15

20 The presence of the deposits in the intake manifold, ports, and on the underside of the intake valve heads leads to a reduction in power output of the engine as a result of throttling the intake fuel-air mixture. With the increasing trend on the part of engine manufacturers to improve volumetric efficiency at high engine speeds, the deleterious effect of these deposits becomes a more serious problem. Additionally, the formation of deposits on the intake manifold surface, which acts as a heat exchanger to improve fuel vaporization, reduces heat transfer and considerably extends the warm-up period of the engine. 25

30 The hydrocarbon components of the gasoline fuel bear no direct relation to the formation of these noted deposits except as the composition of blowby is affected. Tests have indicated that unstable or aged gasolines having high ASTM gum or high potential gum values produce no greater carburetor deposits than stable low-gum gasolines under comparable operating conditions. 30

Deposit formation in fuel injection systems occurs not only in spark-ignition engines, but also in compression ignition engines, such as Diesel engines.

35 With the increased application of compression ignition engines in the field of transportation and power production, greater emphasis has been placed upon improvements in the operating efficiencies of the engine as effected by the fuel composition. It has been recognized that a number of undesirable features in Diesel engine operation, such as increased fuel consumption, excessive exhaust smoking, and certain facets of engine overhauling due to wear, may be in part attributed to the fuel oil and is particularly a function of the deposit-forming characteristics of the fuel oil. 35

40 It has been determined that the presence of deposits on the fuel injector tips alters the normal fuel spray pattern and results in inefficient engine operation due to incomplete fuel combustion. The resulting incomplete combustion of the fuel, occasioned by the presence of deposits in the fuel injection system and the combustion zone, increases the fuel consumption and promotes exhaust smoking, which is particularly objectionable in Diesel trucking operations. In addition, such deposits, when formed in exhaust system passages, cause sparking, which may result in roadside fires. Furthermore, gums and oxidation products in the fuels cause filter clogging. These difficulties are alleviated by the use of the addition agents described hereinbelow. 40

50 It is a particular object of this invention to provide internal combustion engine fuel compositions which are compounded with a metal-free detergent. 50

Therefore, in accordance with this invention, it has been discovered that particularly useful fuel compositions are obtained by incorporating metal-free detergents, that is, polyolefin substituted succinimides of tetraethylene pentamine, in base fuels for internal combustion engines.

55 Thus, the particular succinimides described hereinbelow inhibit deposit formation in internal combustion engine fuel induction systems, providing for more efficient operation of the engine. 55

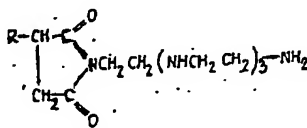
60 The base fuels for spark-ignition engines are fuels in the gasoline boiling range, which include hydrocarbon base fuels boiling essentially in the gasoline boiling range from 100°F. to 450°F., including leaded hydrocarbon base fuels. 60

Ordinarily the base fuels for compression-ignition engines are hydrocarbon base fuels, such as distillate fuels, for example, a mixture of hydrocarbons having a normal distillation range from 300°F. to 750°F., and particularly from 350°F. to 700°F. Such fuels include those derived from various petroleum crude oils, and those derived from

other sources, such as shale oil, or synthetic hydrocarbons obtained from the Fischer-Tropsch process.

The term "leaded hydrocarbon base fuel boiling essentially in the gasoline boiling range" or simply "leaded gasoline", as it is employed in the present description, is intended to designate liquid hydrocarbon fuels boiling in the gasoline boiling range, suitable, accordingly, for use in spark-ignition internal combustion engines and containing lead alkyl additives, such as lead tetraethyl in amounts commonly employed in commercial automotive fuels to prevent occurrence of the engine knock.

The polyolefin substituted succinimides of tetraethylene pentamine have the formula:

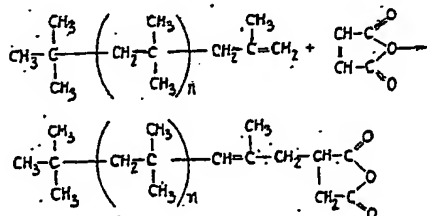


wherein R is derived from a polymer RH of an olefin containing from 2 to 5 carbon atoms, which polymer contains from 30 to 200 carbon atoms.

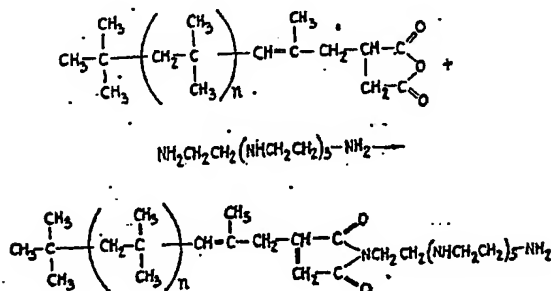
These succinimides of tetraethylene pentamine can be prepared by reacting maleic anhydride with an olefinic polymer, followed by reacting the resulting succinic anhydride with tetraethylene pentamine. The R radical of the above formula is derived from an olefin containing from 2 to 5 carbon atoms by polymerizing an olefin containing from 2 to 5 carbon atoms to form a hydrocarbon having a molecular weight ranging from 400 to 3000, more preferably, 900 to 1200. Such olefins are exemplified by ethylene, propylene, 1-butene, 2-butene, isobutene, and mixtures thereof. Advantageously R may be derived from a polymer of isobutene having a molecular weight of about 1000. Since the methods of polymerizing the olefins to form polymers thereof is immaterial in the formation of the compound described herein, any of the numerous processes available can be used therefor.

The preparation of the succinimides derived from tetraethylene pentamine can be described generally by the following equations, using a polymer of isobutene as an example of the polyolefin RH

I



II



wherein n has a value of 6 to 48.

The above reaction between a polyolefin and maleic anhydride is an uncatalyzed addition reaction which should not be confused with a copolymerization reaction such

as that obtained with a vinyl monomer and maleic anhydride. While the general reaction of an olefin and maleic anhydride is well known for olefins of low molecular weight (e.g., olefins of up to 18 carbon atoms), no previous work has been done with maleic anhydride and the polyolefins as described herein.

The reaction set forth and described by equation I hereinabove can proceed in a mol ratio of the polyolefin to the maleic anhydride of 1:1 to 1:10, preferably from 1:1 to 1:5. The reaction temperature can vary from 300°F. to 500°F. Because of the greater yield of products obtained thereby, it is preferred to use the high range of temperatures (e.g. 430°F. to 470°F.).

In the second step of the reaction as exemplified by equation II hereinabove, the yield of the imide is extremely high even though the reactants are used in equal molar ratios. This is surprising, since under the conditions of the reaction there is an excess of secondary amino groups over primary amino groups, and any reaction with the secondary amino groups would lead to amide formation; thus, preventing imide formation.

The reaction described by equation II hereinabove can be made at 220°F. to 500°F., preferably from 300°F. to 400°F. The succinic anhydride and the tetraethylene pentamine are reacted in about equal molar quantities.

Since the reaction between the polyolefin and maleic anhydride may not go to completion, the resulting succinic anhydride may contain some unreacted polyolefin. As it may not be desirable to separate out this unreacted polyolefin at this stage, the resulting imide formed by reaction of the succinic anhydride and the pentamine will contain this polyolefin as an impurity which can be a diluent in the formation of lubricating oil compositions. However, if it is so desired, this unreacted polyolefin can be removed by precipitation, for example, by acetone or methanol from a hydrocarbon solution.

The succinimides of tetraalkylene pentamine can be used in internal combustion engine fuels in amounts of 25 ppm to 500 ppm or higher, preferably from 100 ppm to 300 ppm. Different fuels require different amounts of the described succinimides. Some fuels may require amounts of 1000 ppm. or higher to 5000 ppm. to give the desired performance characteristics.

The preparation of the polyolefin substituted succinimides of tetraethylene pentamine is illustrated in the following Example.

EXAMPLE

Stage I — Preparation of Polybutene Succinic Anhydride

A mixture of 1000 grams (1 mol) of a polyisobutene having a molecular weight of about 1000 and 98 grams (1 mol) of maleic anhydride was heated at 410°F. in a nitrogen atmosphere with agitation for a period of 24 hours. The reaction mixture was cooled to 150°F. and 700 cc. of hexane added; after which the mixture was filtered under vacuum. After vacuum distillation to remove the hexane from the filtrate, the product was maintained at 350°F. at an absolute pressure of 10 mm. Hg for one hour to remove traces of maleic anhydride. The crude polybutene succinic anhydride thus prepared had a saponification number of 79.

Stage II — Preparation of Tetraethylenepentamine Derivative of the Polybutene Succinic Anhydride of Stage I

A mixture of 84 grams (0.45 mol) of tetraethylene pentamine and 702 grams (0.45 mol) of the polybutene succinic anhydride of Stage I hereinabove, was blended with agitation at 125°F. in a nitrogen atmosphere. The temperature was increased to 400°F. during a period of one hour, after which the absolute pressure was reduced to about 200 mm. Hg during a period of 30 minutes to facilitate the removal of water. The reaction mixture was then allowed to reach room temperature at this reduced pressure. The reaction product contained 4.1% nitrogen (theory = 5.4%). Infra-red analysis showed that the reaction product was an imide containing a polybutene side chain.

Table I hereinbelow presents data showing the effectiveness of the polyolefin substituted succinimides derived from tetraethylene pentamine as detergents in motor fuel compositions.

A laboratory test to facilitate observation and evaluation of carburetor deposits was developed. In this test, standard six-cylinder Ball and Ball Carter Carburetor (D6H2) was modified by removing the throttle plate and shaft from the throttle body. The shaft holes and the transfer port were plugged. A glass throttle body was inserted between the carburetor body and the original throttle body. This glass body consisted of a 1.50-inch I.D., 1.75-inch O.D. Truebore Tubing 1.75 inches long. The original

throttle shaft and plate were installed by drilling holes in the glass and filling the holes to shaft diameter with plastic cement. The engine employed was that of a 6-cylinder Plymouth automobile.

The engine was operated for one hour with the blowby connected to intake air, using a non-detergent base fuel. An automatic cyler provided for 7.5 minute idle periods at 500 rpm. followed by five accelerations to 2000 rpm. The throttle body was removed and both sides were photographed.

The dirty throttle body was then replaced on the engine, with the blowby disconnected from the carburetor. The engine was then run for four hours on the detergent containing test fuel, using the same 7.5 minute idle periods at 500 rpm followed by five accelerations to 2000 rpm. The throttle body was again photographed as before.

The effectiveness of the detergent-containing test fuel was measured by the per cent removal of the base fuel deposits from the throttle body by comparing the photograph of the test fuel run with the photograph of the base fuel run.

The base fuel employed was a commercial leaded (tetraethyl lead) regular gasoline which is representative of nationally available commercial gasolines. As was previously mentioned, the hydrocarbon composition of the base fuel has a negligible effect upon the formation of carburetor deposits, except as it influences the composition of the blowby. Therefore, the test results given in this specification on the base fuel will be approximately the same as for other commercial fuels, irrespective of the stability, gum content or other characteristics of the hydrocarbon components of the fuels.

The succinimide used in the test fuels was a polyolefin substituted succinimide as described in Example II hereinabove, which was a polyolefin substituted succinimide derived from tetraethylene pentamine, wherein the polyolefin had a molecular weight of about 1000 and was a polymer of isobutene.

TABLE I

Succinimide Concentration (ppm)	Glass Throttle Body Cleaning (%)
1. 100	10 (average of 3 tests)
2. 250	50 (average of 2 tests)
3. 500	60 (average of 2 tests)

Table II hereinbelow presents further data showing the advantages obtained with Diesel fuel composition containing the succinimides described herein. These data were obtained in a test designed to measure the effect of additives in preventing the formation of deposits in the injector.

The test was run in a single cylinder diesel engine having Bosch injection equipment. The engine was a modified ASTM—CFR Cetane engine. The injector nozzle was of the single hole pintle-type. The nozzle plunger was used for the rating of the fuel.

The engine was run for 6 hours at 900 rpm, with a fuel rate of 30 ml. in 60±0.6 seconds, an intake air temperature of 100±3°F., and an oil temperature of approximately 140°F. Before the test, a reflectometer was used to measure the light reflected from the pressure differential area of the clean plunger. It was also necessary to get the reflectometer rating of the adapter which holds the plunger. After the test, the dirty plunger was washed with a petroleum thinner, and then the dirty rating was obtained on the reflectometer. The plunger deposit rating is calculated as follows:

$$\% \text{ Deposit} = 100 \times \frac{(\text{Clean rating-adapter rating}) - (\text{Dirty rating-adapter rating})}{(\text{Clean rating-adapter rating})}$$

The base fuel was a light cycle oil from a catalytic cracker having a Cetane number of 36 and a sulfur content of 0.5%. The D—158 Distillation showed an initial point at 430°F., a 50% point at 501°F., and an end point of 596°F.

The additives which were each used in an amount of 200 ppm are described as follows: Additive "A" was a commercially available detergent for fuels, and Additive "B" was an N-substituted succinimide as exemplified by the product of Example II hereinabove.

TABLE II

Additive	Per Cent Deposition
Base Fuel	100.0
Base Fuel + Additive "A"	84.6 (1)
Base Fuel + Additive "B"	66.6 (2)

(1) Average of 13 tests

(2) Average of 4 tests

Tables III and IV hereinbelow illustrate the stability of the succinimides described herein as Diesel fuel Additives.

In the test, the fuel being evaluated was first passed through a filter having a pore size of 0.45 micron. The filtered fuel was then blended with the desired additives. Samples of the base fuel and the compounded fuels were then placed in open 8-inch test tubes in an oil bath at the desired temperature for the period of time of the test. The test samples were cooled to room temperature, and filtered. The filter residue was determined gravimetrically and expressed as parts per million (ppm) of the amount of fuel filtered.

The base fuels for Tables III and IV were the same as that described for Table II hereinabove.

The succinimide was the same as described hereinabove for Tables I and II. The Tests in Table III were conducted for 24 hours at 250°F. with a 1 hour cooling down time.

TABLE III

Fuel	Additive Concentration ppm	Filter Residue ppm
1. Base Fuel	0	140
2. Base Fuel + succinimide	25	136
3. " " "	50	114
4. " " "	75	81
5. " " "	100	43
6. " " "	150	22
7. Base Fuel + (1)	25	160
8. Base Fuel + (1)	100	119
9. Base Fuel + (1)	150	114

(1) Commercially available Additive

The filter residue tests for Table IV were run for 24 hours at 225°F., with a 24 hour cooling down time.

TABLE IV

Fuel	Additive Concentration ppm	Filter Residue ppm
1. Base Fuel	0	50.5
2. Base Fuel+succinimide	25	4
3. " " "	50	2.3
4. " " "	100	2.8

The filter residue test data of Table V hereinbelow were obtained by heating the test samples at 200°F. for 24 hours, with a cooling down time of 1 hour.

The base fuel consisted of 25% of a Gilsonite Coker Distillate derived from Gilsonite Shale, and 75% of a diesel fuel sold by the Utah Oil Company. The word "Gilsonite" is a Trade Mark. Physical characteristics of each of these fuels is described as follows:

	Utah Oil Co. Fuel	Gilsonite
Viscosity at 100°F.SSU	36	37
Cetane No.	36	29—30
D—158 Distillation °F.		
Start	406	415
50% Point	537	463
End Point	698	654

The succinimide used was the same as that described hereinabove.

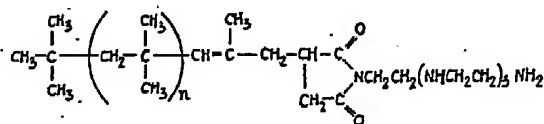
TABLE V

Fuel	Additive Concentration ppm	Filter Residue ppm
1. Base Fuel	0	59
2. Base Fuel + Succinimide	500	4.5

In addition to the subject improving agents in the fuel composition, other conventional fuel additives may be incorporated therein, as, for example, anti-knock or knock-suppressing agents (tetraethyl lead, etc.), surface-ignition suppressants, such as phosphorus-containing compounds, dyes, gum and oxidation inhibitors, provided they are used in such amounts as not to interfere with the beneficial action of the additives of the invention.

WHAT WE CLAIM IS:—

1. An internal combustion engine fuel composition comprising a major proportion of a motor fuel, and from 25 to 5000 ppm of a polyolefin substituted succinimide of tetraethylene pentamine, wherein the polyolefin substituent is derived from a polymer RH of an olefin containing from 2 to 5 carbon atoms, which polymer contains from 30 to 200 carbon atoms.
2. A fuel composition as claimed in Claim 1, wherein the substituted succinimide of tetraethylene pentamine is present in an amount of from 25 to 500 ppm.
3. A fuel composition as claimed in Claim 2 suitable for use in a spark ignition engine, wherein the motor fuel is a fuel in the gasoline boiling range.
4. A fuel composition as claimed in Claim 2 suitable for use in a compression ignition engine, wherein the motor fuel is a hydrocarbon base compression ignition fuel having a distillation range of from 300°F. to 750°F.
5. A fuel composition as claimed in any preceding claim, wherein the polymer RH has a molecular weight of from 900 to 1200.
6. A fuel composition as claimed in any preceding claim, wherein the succinimide has the general formula:



wherein n is a number having a value of from 6 to 48.

7. An internal combustion engine fuel composition according to Claim 1, substantially as hereinbefore described.

HASELTINE, LAKE & CO.,
Chartered Patent Agents,
28 Southampton Buildings, Chancery Lane, London, W.C.2.,
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1964. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.